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Circular Dichroism of Nickel(II) and Copper(II) Complexes with Optically Active Diamines Containing a Pyrrolidinyl Group

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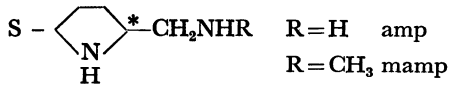
Synopsis. Nickel(II) and copper(II) complexes of diamines containing a (*S*)-pyrrolidinyl group were prepared and their absorption and CD spectra were measured.

Chelating agents with (*S*)-pyrrolidine ring(s) form stereospecific metal complexes, since the nitrogen atom within the pyrrolidine ring coordinates only with the *S*-configuration.[1,2] As an example, *fac*(*N*)-*Λ*-[Ni(L-prolinate)$_3$]$^-$ was predominantly isolated from an aqueous solution containing nickel(II) carbonate and L-proline.[1] In this note, we wish to report the circular dichroism (CD) of nickel(II) and copper(II) complexes with optically active diamines containing a pyrrolidinyl group.

Experimental

From L-proline, the two optically active diamines, (*S*)-2-(aminomethyl)pyrrolidine (abbreviated to amp) and (*S*)-2-(*N*-methylaminomethyl)pyrrolidine (mamp), were prepared *via* their amides by the usual method.[3] Tris(amp)nickel (II) perchlorate was obtained from 1: 3 mixing of nickel(II) perchlorate



and amp in an aqueous solution. Found: C, 32.43; H, 6.59; N, 14.76%. Calcd for [Ni($C_{15}H_{36}N_6$)] (ClO_4)$_2$: C, 32.28; H, 6.50; N, 15.06%. The absorption and CD spectra of the tris(amp) complex were measured in methanol. For the yellow bis-type complexes of amp and mamp, which have a square planar structure, the spectral measurements were carried out as follows. Difinite amounts of nickel(II) perchlorate and each diamine were mixed in a 1: 2 ratio in an aqueous solution. The blue solution was evaporated and dried in vacuo at 50 °C to give a yellow solid. The solid was dissolved in a difinite amount of nitromethane and the spectra were measured. No absorption band originating from an octahedral species was detected in the spectra obtained in this way.

The copper(II) complex of amp was prepared by 1: 2 mixing of copper(II) nitrate and amp and that of mamp by mixing of copper(II) perchlorate and mamp in an aqueous solution. Found for the bis(amp) complex: C, 30.67; H, 6.35; N, 14.31 %. Calcd for [Cu($C_{10}H_{24}N_4$)] (NO_3)$_2$: C, 30.97; H, 6.24; N, 14.45%. Found for the bis(mamp) complex: C, 38.11; H, 7.62; N, 14.53%. Calcd for [Cu($C_{12}H_{28}O_4$)] (ClO_4)$_2$: C, 38.26; H, 7.49; N, 14.87%.

Results and Discussion

In general, the tris((*S*)-diamine) cobalt(III) complex prefers a *Λ*-configuration of *lel*-form(*Λ*-*δδδ*) to a *Δ*-configuration of *ob*-form.[4] A similar situation was assumed in some tris(diamine)nickel(II) complexes.[5,6] The tris complex of amp, which has an asymmetric carbon atom with an *S*-configuration, is also expected to adopt predominantly a *Λ*-configuration.

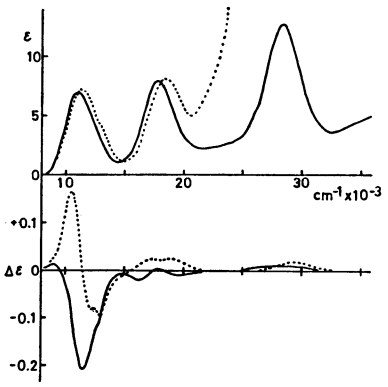


Fig. 1. Absorption and CD spectra of [Ni(amp)$_3$]$^{2+}$ (—) and [Ni((*S*)-3-phenyl-1,2-propanediamine)$_3$]$^{2+}$ (···) in methanol.

Figure 1 shows the absorption and CD spectra of tris(amp)nickel(II) together with those of tris((*S*)-3-phenyl-1,2-propanediamine) complex. The tris(amp) complex exhibits a large negative CD band at the higher wavenumber side and a small positive band at the lower wavenumber side within the region of the first absorption band ($^3A_{2g}\rightarrow{}^3T_{2g}$), which is only one magnetically allowed transition of the three spin-allowed d-d transitions. The CD pattern, a positive component at lower wavenumber and a negative at higher wavenumber, indicates that the complex adopts a *Λ*-configuration as expected.[5,6]

The CD spectra of most of the tris((*S*)-diamine)nickel(II) complexes have a large positive component and a small negative one at the lower and higher wavenumber sides, respectively, in the region of the first absorption band (Fig. 1; Refs. 5 and 6). In the CD curve of the tris (amp) complex, however, the CD magnitudes of the two components are opposite. This is attributable to

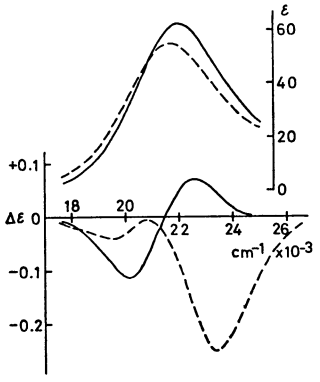


Fig. 2. Absorption and CD spectra of [Ni(amp)$_2$]$^{2+}$ (—) and [Ni(mamp)$_2$] (---) in nitromethane.

the asymmetric nitrogen atom with the *S*-configuration in the pyrrolidine ring. Such a CD curve has also been obtained in the case of tris(L-prolinato)nickel(II).[1]

The absorption and CD spectra of the bis-type yellow complexes of amp and mamp are shown in Fig. 2. The bis(amp) complex exhibits two CD bands, negative at 20200 cm^{-1} and positive at 22500 cm^{-1}. These two bands probably correspond to the two magnetically allowed d-d transitions (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$) of a square planar-type nickel(II) complex. In general, the bis-type yellow complex of *S*-diamine exhibits only one negative CD band at about 22000 cm^{-1} in nitromethane.[7,8] Thus, the appearance of the positive CD band in the bis(amp) complex is due to the asymmetric nitrogen atom in the pyrrolidine ring.

On the other hand, the bis(mamp) complex exhibits only negative CD (Fig. 2). This suggests that another asymmetric nitrogen atom of the methyl-substituted amino group in mamp plays the opposite role in CD sign to the asymmetric nitrogen atom in the pyrrolidine ring. Thus the nitrogen atom of the methylsubstituted amino group in the bis(mamp) complex is expected to have an *R*-configuration.

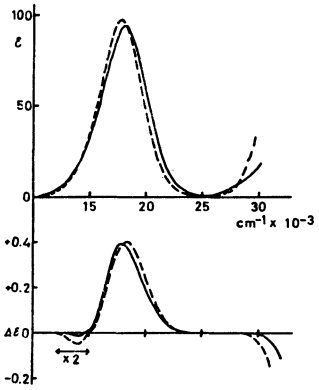


Fig. 3. Absorption and CD spectra of $[Cu(amp)_2]^{2+}$ (—) and $[Cu(mamp)_2]^{2+}$ (---) in water.

Figure 3 shows the absorption and CD spectra of the copper(II) complexes of amp and mamp in aqueous solutions. These two complexes exhibits very similar CD curves which have a main positive CD band at *ca.* 18000 cm^{-1} and a weak negative band at *ca.* 14000 cm^{-1}. Results showing that in some bis(diamine)copper(II) complexes the *N*-substitution of diamine greatly affects the CD spectra have been reported by Morita and Yoshikawa.[9] In the case of mamp, however, the substituted methyl group does not seem to be significant for the CD spectrum of the copper(II) complex. Thus, the *N*-substituted methyl group of mamp may have a different effect on the optical activity of the copper(II) complex from that of the nickel(II) complex.

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